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I, LEANNE MYNOTT, MANAGER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. 2003907205 for a patent by VIROTEC INTERNATIONAL LTD. as filed on 24 December 2003.

I further certify that the above application is now proceeding in the name of MT ASPIRING GEOCHEMISTRY CONSULTANTS PTY LTD pursuant to the provisions of Section 113 of the Patents Act 1990.



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MANAGER EXAMINATION SUPPORT
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PROVISIONAL SPECIFICATION FOR THE INVENTION ENTITLED:

Porous Particulate Material for Fluid Treatment

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This invention is best described in the following statement:

POROUS PARTICULATE MATERIAL FOR FLUID TREATMENT

Technical Field

This invention relates to the treatment of one or more contaminants in a fluid. More particularly, the invention relates to porous particulate material for the treatment of a fluid
5 containing a contaminant and to a process for making such particulate material.

Background of the Invention

Acid mine drainage (AMD) is a well known problem wherever sulphidic mine tailings are stored; it affects most copper, lead, zinc, nickel and silver mining and smelting
10 operations, most gold recovery operations other than those involving placer deposits, many coal mining and beneficiation operations and others. A potential environmental hazard exists wherever human activity involves exposing sulphide minerals to the atmosphere such that the sulphides can oxidise producing acid water that often has a high trace metal content. Some of these trace metals have high ecological toxicities, which are
15 highly detrimental to the environment. Preventing the formation and escape of acidic metal-rich leachate from mineral recovery operations poses a management problem for modern mining operations and a major remediation problem for waste deposits associated with abandoned mining operations. The control of AMD is an expensive activity for both current and former mine sites. The release of acidic metal-rich waters from current and
20 former mine sites is widely considered to be the greatest environmental hazard associated with mining and ore beneficiation operations.

Similarly, many industrial processes also produce acid metal-rich waste streams (eg, tanneries, electro-plating works, fertiliser manufacturing and many others) that require treatment before they can be discharged or disposed of. Many industrial and waste
25 management processes also produce gaseous emissions that contain odour producing compounds or components that can produce acid when they interact with water.

There accordingly exists a need for processes and compositions that can be used for the treatment of large volumes of acidic waters and trace metal-contaminated waters, such as those referred to above, at low cost.

30 Alumina (Al_2O_3) is produced industrially in the Bayer process. The Bayer process uses sodium hydroxide (NaOH) to selectively dissolve the aluminous minerals that are present in bauxite ore. This produces a sodium-aluminate solution from which pure $\text{Al}(\text{OH})_3$ is precipitated. The residues that result from caustic soda digestion of the bauxite ore are commonly known as 'red mud'. Bauxite refinery residues or red mud have a high

ferric iron content and are highly caustic with pH values of about 13.5. In alumina production, large volumes of these highly caustic bauxite refinery residues are produced and can be difficult to dispose of safely and economically.

5 Geochemical studies of bauxite refinery residues have shown that they are dominated by particles with a very high surface area/volume ratio and a high particle charge to mass ratio. These studies have also shown that bauxite refinery residues that have had their pH reduced such that they retain their alkalinity but are not caustic, can neutralise acid and bind many trace elements and other compounds by formation of new low solubility minerals, by coprecipitation with other minerals and by isomorphous
10 substitution for elements in other minerals.

Despite the desirable acid neutralising and metal binding characteristics of red mud, it is difficult to handle, has a high moisture content that substantially increases transport costs, has a very low permeability, and forms a fine red dust when physically broken up when dry. These limitations are not a serious impediment when treating
15 standing waters in remote areas, but they do adversely affect the ability to treat flowing acid waters, metal-rich waters and waters in areas near population centres, as well as gaseous emissions. They further impose major constraints on the use of red mud in permeable reactive barriers or passive water treatment columns or tanks where it is necessary to maintain moderate permeabilities. Clearly, in the form in which it is
20 produced by bauxite refineries, red mud cannot be applied to treat flowing water bodies because the potential loss of fine red mud particles down stream s unacceptable. Furthermore, due to the small particle size of fine red mud particles, they are often not suitable for use in reactive barriers.

25 **Objects of the Invention**

It is an object of the present invention to address or ameliorate at least one of the aforementioned disadvantages or needs.

Summary of the Invention

30 According to a first aspect of the invention, there is provided a porous particulate material for treating a fluid containing a contaminant, the particulate material comprising a cementitious matrix and bauxite refinery residue.

Advantageously, the volume percent of pores within the particulate material is in the range selected from the group consisting of 10% to 90%; 20% to 80%; 30% to 70%; 40% to 60%; or 45% to 55%.

Suitably, at least a portion of the pores in the particulate material may be open cell or interconnected pores. Preferably, at least 10 % of the pores are open cell or interconnected pores. More preferably, the proportion of pores that are open cell or interconnected pores within the particulate material are in the range selected from the group consisting of 10% to 100 %; 20 to 100%; 30 to 100%; 40 to 100%; 50 to 100%; 60 to 100%; 70 to 100%; 80 to 100%; and 90 to 100%.

Advantageously, the pores of the particulate material have a distributed pore size. The pore size of the particulate material may be within the range of 0.1 to 2000 μm . The pores may consist of macro-pores having a pore size in the range of 100 to 2000 μm , mesopores having a pore size in the range of 10 to 100 μm and micro-pores having a pore size in the range of 0.1 to 10 μm . At least some of the macro-pores should be interconnected by meso-pores or micro-pores and at least some of the meso-pores are interconnected by micro-pores.

According to a second aspect of the invention, there is provided a porous particulate material for treating a fluid containing a contaminant, the particulate material comprising a coherent mass of particles, wherein the particles comprise a cementitious matrix and bauxite refinery residue.

Suitably, the particulate material may be present in the form selected from the group consisting of granules, pellets, briquettes, extrudites, gravel, cobbles, blocks, interlocking blocks or slabs.

According to a third aspect of the invention, there is provided a reactive permeable barrier for treating a fluid containing a contaminant comprising a permeable mass of the porous particulate materials according to the first or second aspect or both, wherein in use the permeable mass of the porous particulate materials are disposed within a flow path of the fluid containing the contaminant.

The reactive permeable barrier may be a sub-surface reactive permeable barrier. In other embodiments, the reactive permeable barrier may be located in a vessel such as a column or tank.

According to fourth aspect of the invention, there is provided a composition for forming porous particulate material for treating a fluid containing a contaminant, the composition comprising bauxite refinery residue and a cementitious binder, wherein the

cementitious binder is present in a sufficient quantity to form porous particulate material according to the first or second aspect or both.

Suitably an pore generating agent may be included in the composition to generate pores within the particulate material upon mixing the composition in an aqueous media.

5 The pore generating agent may be selected from the group selected from, but not limited to, hydrogen peroxide, organic polymers and foaming agents.

According to a fifth aspect of the present invention, there is provided a method for producing porous particulate material for treating a fluid containing a contaminant, the particulate material comprising a coherent mass of particles, the method comprising:

- 10 (a) mixing bauxite refinery residue and cementitious binder in aqueous media to form a slurry;
- (b) curing the slurry within a defined temperature range and for a defined period of time to form porous particulate materials having a cementitious matrix and bauxite refinery residue.

15 According to a sixth aspect of the present invention, there is provided a method for producing a porous particulate material for treating a fluid containing a contaminant, the particulate material comprising a coherent mass of particles, the method comprising:

- (a) mixing bauxite refinery residue and cementitious binder in aqueous media to form a slurry;
- 20 (b) curing the slurry in a mould to form a coherent mass of porous particulate material having a cementitious matrix and bauxite refinery residue.

The mould may be shaped to form a coherent mass of porous particulate material in the form selected from the group consisting of granules, pellets, briquettes, extrudites, gravel, cobbles, blocks, interlocking blocks or slabs.

25 Suitably a pore generating agent may be added in the mixing step to generate pores within the particulate material. The pore generating agent may be selected from the group selected from, but not limited to, hydrogen peroxide, organic polymers, foaming agents, and gasses such as air.

Suitably, a phosphorising agent may be added to assist in stabilisation of the pore
30 structures during curing. The phosphorising agent may be phosphoric acid.

The slurry may be allowed to cure for a period of from 1 day to 60 days, preferably from 1 day to 50 days, more preferably from 1 to 30 days.

According to a seventh aspect of the present invention, there is provided a method for treating a fluid containing a contaminant, the method comprising :

providing a permeable mass of porous particulate materials according to the first or second aspect or both; and

passing the fluid containing the contaminant through the permeable mass of porous particulate materials.

5 The fluid may be a contaminated water or a contaminated gaseous fluid. The contaminant in the fluid may be selected from the group consisting of, but not limited to, acids; metal ions such as lead, aluminium, beryllium, cadmium, chromium, cobalt copper, iron, nickel, manganese, mercury, silver, zinc; metalloids such as antimony or arsenic; and anions such as borate, carbonate, cyanide, metal oxyanion complexes, oxalate
10 phosphate, sulfate, halides, and ; gasses such as carbon dioxide, nitric oxide, nitrous oxide, sulphur dioxide, sulphur trioxide, ; and one or more combinations thereof.

The composition of the slurry may comprise from 1% to 99% w/w of bauxite refinery residue and from 1% to 99% of a cementitious binder. A preferred composition includes from 50% to 95% by dry weight of bauxite refinery residue and from 5% to 50%
15 by weight of cementitious binder. A more preferred composition includes from 70% to 90% by weight of bauxite refinery residue and from 10% to 30% by weight of cementitious binder, and a most preferred composition comprises from 80% to 85% by dry weight of the bauxite refinery residues and from 15% to 20% by weight of cementitious binder. Advantageously, additional additives may be added to the bauxite
20 refinery residue, the additional additives selected from the group consisting of sand and ground caustic steel slag residue, alkali metal hydroxides such as sodium hydroxide, alkali metal carbonates such as sodium carbonate, alkaline earth metal hydroxides such as calcium hydroxide, alkaline earth metal carbonates such as calcium carbonate, alkaline earth metal oxides such as magnesium oxide, calcium hypochlorite, sodium alum, ferrous
25 sulfate, ferric sulphate, ferric chloride, aluminium sulfate, gypsum, phosphates such as ammonium phosphate, phosphoric acid, hydrotalcite, zeolites, olivines and pyroxenes (including those present in basic and ultra basic igneous rocks) barium chloride, silicic acid and salts thereof, meta silicic acid and salts thereof, jarosite or other alunite group minerals and magadiite and one or more combinations thereof. The additional additives
30 may be added to the slurry provide a composition with an enhanced acid neutralising capacity or an enhanced ability to remove a specific contaminant in the fluid.

Suitably, the bauxite refinery residues have a pH less than about 10.5. Preferably, the bauxite refinery residues have a pH in the range between about 8 and about 10.

A cementitious binder capable of forming a tobermorite gel is preferred. A preferred cementitious binder is a cement selected from the group consisting of normal portland cement, high early strength portland cement, low heat portland cement, sulphate resisting portland cement, and high alumina cements, or any other commercially available cementing agent that relies on the development of tobermorite gels.

Optionally, additives may be added to the cementitious binder to improve geochemical, physical or other characteristics. Additives may comprise a compound selected from a silica provider, a plasticiser, a polymeriser, a phosphatising agent, an air entraining agent, or a combination of any two or more of the foregoing.

Preferred plasticisers are cellulose -based plasticisers such as hydroxypropyl methyl cellulose (HPMC). An organic type plasticiser that may be used is dibutyl phthalate (DBP).

Definitions

In the context of this specification, the term "comprising" means "including principally, but not necessarily solely". Furthermore, variations of the word "comprising", such as "comprise" and "comprises", have correspondingly varied meanings.

The term "red mud" hereafter may include "treated red mud", "partially treated red mud", "untreated red mud" and bauxite refinery residue.

The term "treated red mud" hereafter means red mud that has a pH less than 10.5.

The term "partially treated red mud" hereafter means red mud that has a pH in the range of 10.5 to less than 13.5. The term "untreated red mud" means red mud that has a pH of 13.5 or more.

Brief Description of the Drawings

In the accompanying drawings, Figures 1 through to 6 are Scanning Electron Microscope (SEM) images of pellets of a composition according to the invention; as follows:

Figure 1 is an SEM image of one pellet of a composition according to the invention, showing the distribution of macro-pores developed during pelletisation thereof;

Figure 2 is an SEM image of the pellet of Figure 1; showing the detail of fine pores therein;

Figure 3 is an SEM image of the pellet of Figures 1 and 2, showing a fine interconnected tobermorite gel forming part thereof;

Figure 4 is an SEM image of the pellet of Figures 1 to 3, showing the collapsed tops of two carbonate filled macro-pores;

5 Figure 5 is an SEM image of another pellet of a composition according to the invention, showing the distribution of macro-pores developed during the pelletisation process; and

Figure 6 is a high resolution SEM image of the surface of the pellet of Figure 5, showing a micro-pore network that permeates the pellet.

10 Figure 7 shows a schematic diagram of an exemplary laboratory apparatus that was used to obtain the results disclosed in example 2 below.

Figure 8 shows a schematic diagram of an exemplary industrial process to treat contaminated water using pellets having a composition according to the invention.

15 Figure 9 shows cross-sectional view of a sub-surface permeable reactive barrier that utilises pellets according to the invention.

Detailed Description of the Invention

Red mud

20 The treatment of the red mud may comprise a treatment with calcium and/or magnesium ions so as to yield a substance that has a reaction pH of less than 10.5 when mixed with water in a weight ratio of red mud to water of 1:5. Alternatively, the treatment of the red mud may comprise neutralisation thereof by the addition of acid. As another alternative, the treatment of the red mud may comprise contact with carbon dioxide; or the addition of a mineral such as gypsum.

25 The treated red mud may be red mud that has been activated by acid treatment neutralisation and calcination or red mud that has been chemically and/or physically altered in any other way such as by washing with water or size separation.

30 The red mud may be at least partially reacted with calcium and/or magnesium ions so as to have a reaction pH, when mixed with 5 times its weight of water, of less than 10.5 to become treated red mud. More preferably the reaction pH, when mixed with 5 times its weight of water, is less than a value selected from the group consisting of about 10, about 9.5, about 9, about 8.5 and about 8. The reaction pH of treated red mud, when mixed with 5 times its weight of water, may be about 8 – 10.5, alternatively about 8.5 - 10, alternatively about 8 – 8.5, alternatively about 8 - 9, alternatively about 8.5 - 9.5,

alternatively about 9 - 10, alternatively about 9.5 - 10, alternatively about 9 - 9.5, and may be about 10.5, 10, 9.5, 9, 8.5 or 8.

One method by which treated red mud, as defined herein, may be prepared is by reacting untreated or partially treated red mud with calcium and/or magnesium ions as described in International Patent Application No. PCT/AU03/00865 and International Patent Application No. PCT/AU01/01383, the contents of which are incorporated herein in their entirety. Another way in which treated red mud may be prepared is by reaction of untreated or partially treated red mud with sufficient quantity of seawater to decrease the reaction pH of the red mud to less than 10.5. For example, it has been found that if an untreated red mud has a pH of about 13.5 and an alkalinity in the liquid phase of about 20,000 mg/L, the addition of about 5 volumes of world average seawater will reduce the pH to between 9.0 and 9.5 and the alkalinity to about 300 mg/L.

As taught in International Patent Application No. PCT/AU03/00865 and International Patent Application No. PCT/AU01/01383, a process for reacting untreated or partially treated red mud with calcium and/or magnesium ions may comprise mixing untreated or partially treated red mud with an aqueous treating solution containing a base amount and a treating amount of calcium ions and a base amount and a treating amount of magnesium ions, for a time sufficient to bring the reaction pH of the red mud, when one part by weight is mixed with 5 parts by weight of distilled or deionised water, to less than 10.5. The base amounts of calcium and magnesium ions are 8 millimoles and 12 millimoles, respectively, per litre of the total volume of the treating solution and the red mud; the treating amount of calcium ions is at least 25 millimoles per mole of total alkalinity of the red mud expressed as calcium carbonate equivalent alkalinity and the treating amount of magnesium ions is at least 400 millimoles per mole of total alkalinity of the red mud expressed as calcium carbonate equivalent alkalinity. In addition to the possible use of seawater, as taught in International Patent Application No. PCT/AU03/00865 and International Patent Application No. PCT/AU01/01383, examples of sources of calcium and magnesium include hard groundwater brines, natural saline brines (e.g. evaporatively concentrated seawater, bittern brines from salt mines or salt lake brines), saline wastewaters (e.g. from desalination plants), and solutions made by dissolving calcium chloride and magnesium chloride. However, sources of calcium and/or magnesium ions are not limited to these examples.

A further method by which treated red mud may be prepared comprises the steps of:

(a) contacting the untreated or partially treated red mud with a water soluble salt of an alkaline earth metal, typically calcium or magnesium or a mixture of the two, so as to reduce at least one of the pH and alkalinity of the red mud; and

(b) contacting the untreated or partially treated red mud with an acid so as to reduce the pH of the red mud to less than 10.5.

In step (b), the pH of the red mud may be reduced to about 8.5 - 10, alternatively to about 8.5 - 9.5, alternatively to about 9 - 10, alternatively to about 9.5 - 10, preferably from about 9 - 9.5, and may be reduced to a value selected from the group consisting of about 10.5, about 10, about 9.5, about 9, about 8.5 and about 8.

In step (a) of this process, the total alkalinity of the liquid phase, expressed as calcium carbonate alkalinity, of the red mud may be reduced to about 200 mg/L - 1000 mg/L, alternatively to about 200 mg/L - 900 mg/L, alternatively to about 200 mg/L - 800 mg/L, alternatively to about 200 mg/L - 700 mg/L, alternatively to about 200 mg/L - 600 mg/L, alternatively to about 200 mg/L - 500 mg/L, alternatively to about 200 mg/L - 400 mg/L, alternatively to about 200 mg/L - 300 mg/L, alternatively to about 300 mg/L - 1000 mg/L, alternatively to about 400 mg/L - 1000 mg/L, alternatively to about 500 mg/L - 1000 mg/L, alternatively to about 600 mg/L - 1000 mg/L, alternatively to about 700 mg/L - 1000 mg/L, alternatively to about 800 mg/L - 1000 mg/L, alternatively to about 900 mg/L - 1000 mg/L, preferably less than 300 mg/L, and may be reduced to less than a value selected from the group consisting of about 1000 mg/L, about 900 mg/L, about 800 mg/L, about 700 mg/L, about 600 mg/L, about 500 mg/L, about 400 mg/L, about 300 mg/L and about 200 mg/L or may be reduced to a value selected from the group consisting of about 1000, about 950, about 900, about 850, about 800, about 750, about 700, about 650, about 600, about 550, about 500, about 450, about 400, about 350, about 300, about 250 and about 200 mg/L.

The pH is typically reduced to less than about 9.5, preferably to less than about 9.0, and may be reduced to a value selected from the group consisting of about 9.5, about 9.25, about 9.0, about 8.75, about 8.5, about 8.25 and about 8 and the total alkalinity of the liquid phase, expressed as calcium carbonate equivalent alkalinity, is preferably reduced to less than a value selected from the group consisting of about 200 mg/L, about 150 mg/L and about 100 mg/L, and may be reduced to a value selected from the group consisting of about 200, about 175, about 150, about 125, about 100, about 75 and about 50 mg/L.

As described in International Patent Application No. PCT/AU03/00865 and International Patent Application No. PCT/AU01/01383, treated red mud, as defined herein, is a dry red solid that consists of a complex mixture of minerals that usually includes: abundant hematite, boehmite, gibbsite, sodalite, quartz and cancrinite, minor
5 aragonite, brucite, calcite, diaspore, ferrihydrite, gypsum, hydrocalumite, hydrotalcite, p-aluminohydrocalcite and portlandite, and a few low solubility trace minerals. It has a high acid neutralising capacity (2.5 - 7.5 moles of acid per kg of treated red mud) and a very high trace metal trapping capacity (greater than 1,000 milliequivalents of metal per kg of treated red mud); it also has a high capacity to trap and bind phosphate and some other
10 chemical species. Treated red mud can be produced in various forms to suit individual applications (e.g. slurries, powders, pellets, etc.) but all have a near-neutral soil reaction pH (less than 10.5 and more typically between 8.2 and 8.6) despite their high acid neutralising capacity. The soil reaction pH of treated red mud is sufficiently close to neutral and its TCLP (Toxicity Characteristic Leaching Procedure) values are sufficiently
15 low that it can be transported and used without the need to obtain special permits.

A preferred treated red mud is available from Virotec International Pty Ltd of Sanctuary Cove, Queensland, Australia, under the trademark Bauxsol™.

It will be appreciated from the foregoing, however, that the red mud for use in the compositions and methods of the present invention is not limited to treated red mud,
20 as herein defined, and may also be red mud that has been at least "partially treated" (ie has a pH between 10.5 and 13.5) by treatment with acid; red mud that has been at least partially treated by treatment with carbon dioxide; or red mud that has been at least partially treated by addition of one or more minerals containing calcium and/or magnesium (such as gypsum). Red mud may conveniently be at least partially treated by
25 treatment with carbon dioxide, by bubbling carbon dioxide into an aqueous suspension of red mud, or by injecting carbon dioxide into such a suspension under pressure, until the reaction pH of the red mud is decreased to less than a value selected from the group consisting of between 10.5 and 13..

The typical mineralogy and chemical composition of treated red mud is
30 summarised in Table I below.

TABLE I		
Typical treated red mud composition		
	% Unwashed Mean	(%) Washed Mean
Iron oxides ¹ & oxyhydroxides	31.6	33.2
Hydrated alumina ²	17.9	18.1
Sodalite	17.3	17.8
Quartz	6.8	7.0
Cancrinite	6.5	6.5
Titanium oxides ³	4.9	5.0
Ca(Al) hydroxides & hydroxycarbonates ⁴	4.5	4.6
Mg(Al) hydroxides & hydroxycarbonates ⁵	3.8	3.9
Calcium carbonates ⁶	2.3	2.2
Halite	2.7	0.03
Others ⁷	1.7	1.7

The texture and mineralogy of treated red mud give it a very high trace element trapping and binding capacity (>1000 meq/kg, at pH values >6.5) and the ability to strip trace elements from water in contact with it. The metal binding property of treated red mud becomes stronger as it ages. In addition to the high metal binding capacities, treated red mud has an acid neutralising capacity that is greater than 3.5 moles of acid per kg of dry treated red mud and is usually greater than 4.5 moles of acid per kg of dry treated red mud. These properties make treated red mud suitable for a wide range of water treatment and other similar applications.

¹ Iron oxides & oxyhydroxides include hematite & ferrihydrite.

² Hydrated alumina includes: boehmite & gibbsite (mainly boehmite).

³ Titanium oxides include: anatase & rutile

⁴ Ca(Al) hydroxides & hydroxycarbonates include: hydrocalumite & p-aluminohydrocalcite.

⁵ Mg(Al) hydroxides & hydroxycarbonates include: brucite & hydrotalcite

⁶ Calcium carbonates include: calcite & aragonite

⁷ "Others" include: diaspore, lepidocrocite, portlandite, chromite, monazite, zircon, fluorite, euxinite, gypsum, anhydrite, bassanite, whewellite.

The mineral constituents of treated red mud are non-toxic to humans and animals either individually or collectively. Many of the minerals present in treated red mud are used in pharmaceutical products for human consumption.

The treated red mud or partially treated red mud is preferably finely ground.

5 A method for forming treated red mud is described in PCT AU03/00865. The resulting treated red mud has the typical mineralogy and chemical composition summarised in Table I.

10 A particular benefit of using treated red mud in the composition and process of the invention is that the soluble salt concentrations, especially sodium concentrations, are substantially lower than those in untreated red mud. This feature of treated red mud is particularly important where the salinity of treated must be low such as where the water is to be discharged to the environment or where it is to be used for irrigation purposes or as drinking water for mammals.

15 **Cementitious Binder**

The cementitious substance may be a tobermorite gel. Most typically tobermorite gel is produced in the setting of industrial cements and includes, but need not be limited to (normal portland cement, high early strength portland cement, low heat portland cement, sulphate resisting portland cement, and high alumina cements, or any other commercially
20 available cementing agent that relies on the development of tobermorite gels) and is hereinafter referred to as "cement". Within a tobermorite gel, four main constituents are present, these are: tricalcium silicate (C_3S), dicalcium silicate (C_2S) tricalcium aluminate (C_3A) and tetracalcium alumino-ferrate (C_4AF).

25 The incorporation of organic additives during pellet formation can provide additional binding strength by producing a fibrous mat, while the xylem and phloem of the tissue can provide additional interconnecting pathways for fluid flow. In addition, organic matter provides a suitable bacteria growth medium, so that formed pellets may be used in anaerobic treatments that will allow biogeochemical reactions (eg sulphate reduction, and denitrification) to progress efficiently. Furthermore, organic matter within
30 the pellets can provide additional nutrient and carbon sources for plant growth, should pellets be used in soil remediation programs or potting mix extenders. Organic matter that may be incorporated into pellets may include, but should not be limited to, sewage biosolids, sugarcane crushing residues, straw chaff, mulches, and hemp fibre, etc. The preferred range of added organic matter would be in the range of 0% to 15% by weight of

the dry mixture, the more preferred range of 0.4% to 10% by weight of the dry mixture, the even more preferred range of 0.6% to 8% by weight of the dry mixture and a most preferred range of 0.8% to 5.0% by weight of the dry mixture.

5 Mineral additives

The operational benefits of the treated red mud can frequently be enhanced by the addition of mineral additives as taught in PCT/AU01/01383. Possible additives include one or more substances selected from the group consisting of alkali metal hydroxides (e.g. sodium hydroxide), alkali metal carbonates (e.g. sodium carbonate), alkaline earth metal hydroxides (e.g. calcium hydroxide), alkaline earth metal carbonates (e.g. calcium carbonate), alkaline earth metal oxides (e.g. magnesium oxide), calcium hypochlorite, sodium alum, ferrous sulfate, ferric sulphate, ferric chloride, aluminium sulfate, gypsum, phosphates (e.g. ammonium phosphate), phosphoric acid, hydrotalcite, zeolites, olivines and pyroxenes (including those present in basic and ultra basic igneous rocks), barium chloride, silicic acid and salts thereof, meta silicic acid and salts thereof, jarosite or other alunite group minerals and magadiite. One or more of these substances can be added to the mixture to be pelletised to enhance particular properties of the pellets. The preferred range of addition rates for any one mineral additive would be in the range of 0% to 30% by weight of the dry mixture, the more preferred range of 1% to 25% by weight of the dry mixture, the even more preferred range of 2% to 20% by weight of the dry mixture and a most preferred range of 5% to 15% by weight of the dry mixture. It should be understood that the addition of mineral additives will reduce the amount of red mud used.

Slurry Water

If added in a suitable proportion, and mixed with a dry cementitious substance, water causes it to form a tobermorite gel. This is useful for pellet formation. However, if too little water is added, the resulting tobermorite gel sets into a solid substance that has an undesirably high level of macro-porosity and is of low strength, whilst, if too much water is added, the resulting tobermorite gel sets into a solid substance that has a low pore size distribution, lowered permeability and poor drying characteristics.

It is preferable to have the mixture slightly too wet than to have the mixture slightly too dry. Water should be added to the dry ingredients and blended till a smooth paste develops. The preferred range of water to be added depends on the treated red mud

blend used, the proportion of acid neutralising hydroxide and oxide minerals present in the blend, and the initial water content of the treated red mud.

When treated red mud and portland cement is used as the binder, the preferred range for water addition is from 15% to 55% water to dry ingredients by weight, with a more preferred range of 25% to 45% water to dry ingredients by weight, with an even more preferred range of 30% to 40% water to dry ingredients by weight, and a most preferred range of 33% to 37% water to dry ingredients, by weight. However, the optimum amount of water will also depend on the moisture content of the red mud used (this may vary between batches) and consequently, the exact amount of water to be added will be determined by operator experience.

Silica Providers

Other components may be included in the mix to provide additional silica sources for tobermorite gel formation and may include, but not be limited to silica sand, diatomite, fly ash, bottom ash, and crushed silicate rock, which may be added either alone or as combinations. The preferred range these added silica sources would be in the range of 0% to 30% by dry weight, the more preferred range of 3% to 20% by dry weight, and a most preferred range of 5% to 12% by dry weight.

Plasticisers and polymerisers

Plasticisers and/or polymerisers may also be added to the composition to facilitate pellet formation, to provide greater workability of the wetted mixture, to inhibit initial setting times, to provide additional binding strength to the cured product, and/or to provide a wettable surface for water to penetrate along pores into cured pellets, so as to prevent pellet slaking.

Plasticisers and polymerisers include, but should not be limited to cellulosic substances, such as methyl-hydroxyethyl-cellulose (MHEC) and hydroxypropyl-methyl-cellulose (HPMC) and polymerising agents such as dibutyl phthalate (DBP).

Highly substituted organic plasticisers and polymerisers are preferred for the addition to the pellet mixtures using treated red mud blends (eg HPMC), whereas in low ionic strength systems (eg freshwater rinsed treated red mud) less highly substituted plasticisers/polymerisers may be used (eg MHEC); salting out (excessive salt loading) of the plasticiser reduces plasticiser performance. The preferred plasticiser addition rate is from about 0.01% to about 8% by weight of the dry mixture, a preferred range being

about 0.4% to about 5% by weight of the dry mixture, whilst an even more preferred range is about 0.6% to about 3% by weight of the dry mixture . A most preferred range is from about 0.8% to about 2.0% by weight of the dry mixture.

5 Air Entraining Agents

The entrainment of air provides the porosity and permeability within pellets. Air may be entrained in one or both of two methods. Firstly, physical mixing of the slurry entrains small gas bubbles and secondly, air entraining agents either release gases under the chemical conditions of the slurry, or aid in the incorporation of air during slurry mixing. Air entraining agents may include hydrogen peroxide, organic polymers and commercially available organic foaming agents.

Hydrogen peroxide becomes unstable under the chemical conditions of the slurry and breaks down to evolve oxygen that expands to provide porosity. The upward migration of gas bubbles provides pellet permeability (the interconnection of porosity).

Hydrogen peroxide as an air entraining agent may be used in varying strengths, preferably in the range of 0.1% to 75% weight to volume hydrogen peroxide, more preferably between 1% to 30% weight to volume hydrogen peroxide, and most preferably between 3% to 10% weight to volume hydrogen peroxide. For a 3% weight to volume hydrogen peroxide, addition rates are preferably between 1 mL to 25 mL per kg of dry mixture, more preferably between 2 mL to 20 mL per kg of dry mixture, and even more preferably between 5 mL to 15 mL per kg of dry mixture, and most preferably between 8 mL to 10 mL per kg of dry mixture. Higher addition rates or higher concentrations of the air entraining agent provide greater porosity and permeability, but lower physical strength.

25 Phosphatising Agents

The development of apatite like minerals within pellets and phosphate cross linking between mineral crystals may provide additional strength benefits, especially wet strength, which in combination with the air entraining agents aids micro-porosity development and stability. Phosphate may also act to trap and bind heavy metals. Phosphatising agents may be added to the pellet mixture and may include phosphoric acid, tri-sodium phosphate, di-sodium hydrogen-phosphate, sodium di-hydrogen phosphate, tri-potassium phosphate, di-potassium hydrogen-phosphate, potassium di-hydrogen phosphate.

The phosphatising agent may be phosphoric acid. The phosphoric acid may have a strength between about 0.01M and about 18M, preferably between about 0.1M and about 5M, more preferably between about 0.5M and about 3M, and even more preferably between about 1M and about 2M. At a phosphoric acid strength of 1.5M, the preferred addition rate may be 0.2 mL to 4 mL per kg of dry ingredients, preferably about 1 mL to about 3.5 mL per kg of dry ingredients, more preferably about 1.5 mL to about 2.5 mL per kg of dry ingredients, even more preferably about 2 mL to about 2.5 mL per kg of dry ingredients.

10 Mixing

The dry materials may be sieved, preferably to <2 mm, more preferably to <1 mm, even more preferably <500 μ m and most preferably <250 μ m, and fully mixed to reduce material clumping, before the introduction of water or any other wet material such as an aqueous solution comprising the phosphatising agent and/or the air entraining agent.

15 The wet materials are preferably mixed together before addition to dry materials, but they may be added individually. If the wet ingredients are to be mixed with the dry ingredients individually then the preferred mixing order is to add water to the dry materials before the phosphatising agent or the air entraining agent is added.

Over mixing of the slurry (ie, going from a slightly wet to slightly dry slurry) to ensure a complete entrainment of air during the mixing process is preferred. Mixing should preferably proceed until air entrainment is complete because air entrainment is substantially reduced once mixing is stopped.

Mixing can be achieved by various means, including commercially available shear-force mixers, and concrete mixers that turn over material. With mixing, the slurry material is preferably folded in on itself for at least 5 minutes, preferably at least for about 10 minutes at a rate of at least 10 times per minute, more preferably at about 20 times per minute, and even more preferably at about 30 times per minute (expressed as standard revolutions per minute for commercially available concrete mixers). Shear-force mixers (eg bread mixers) typically operate at higher mixing rates than standard concrete mixers, and depending on the machine specifications, mixing times may be adjusted accordingly.

Pellet Moulding and Drying

The strength of a tobermorite gel continues to increase with time, for a period lasting several months, and even years. After about 28 days, further increases in strength

occur increasingly slowly. Initial setting of cement is achieved by the development of the C_3A and C_4AF forms of tobermorite, over a period of 0-10 days, the C_3S and C_2S tobermorite gel forms over the period of 0-400 days.

5 Slab Casting

The composition according to the invention may be cast in slabs. Slab pouring may require a mixer of sufficient volume (eg batching works off road works) with accurate scales, and an IBC mixer for mixing of plasticiser etc. Screening of all products may be necessary so a vibrating screen may be used above the mixer entry point for the
10 cement, lime, magnesium oxide.

Treated red mud slurry may be pumped through a wet screen prior to addition to the mixer. Slab making may require a back-hoe for slab transportation and a crane where lifting hooks are to be moulded into the slab. Slabs may be stacked for storage, and may be allowed to dry in a shed before crushing, and then transported in bulk or in bags etc.
15 Slabs may be transported whole and may be crushed on site. Slabs may be stored in open weather.

Crushing

Once cured, the slabs or coarse pellet blocks may be crushed or mechanically
20 chipped or cut/sheared and graded to provide pellets of any desired size. Pellets are preferably crushed to a size of less than about $1/10^{\text{th}}$ of the internal diameter of the column that they are to be packed in, more preferably to a size of less than about $1/20^{\text{th}}$ of the internal diameter of the column, even more preferably to a size of less than about $1/40^{\text{th}}$ of the internal diameter of the column, and most preferably to a size of less than
25 about $1/50^{\text{th}}$ of the internal diameter of the column.

Typically, the crushed pellets will have a size distribution in a preferred range of about 0.05 mm to 100 mm, with a more preferable size distribution range of about 0.1 mm to about 10 mm, a more preferred size distribution range of about 0.2 mm to about 5 mm, and a most preferred size distribution range of about 0.5 mm to about 2.5 mm.
30 However, pellets with very different size ranges may be selected for particular applications as required. For example, large particles (cobble size) may be required for use in stream bed applications, whereas pellets with sizes between 0.5 mm and 2 mm may be the most suitable for small water treatment columns.

Formation of particles

The compositions of the invention may be provided in the form of a particulate blend or they may be provided as granules, pellets, tablets, bricks, chunks or blocks composed of the mixed components depending on the crushing or cutting procedures used. Preferably, the compositions of the invention are provided in the form of pellets made from an intimate mixture of the components of the composition. Any coarse particles are preferably crushed, cut/sheared or ground. After said crushing, cutting or grinding, particles are sieved or screened to provide the desired size range for each application. Sizes will typically be in the range 0.05mm to 10cm. However, as a result of crushing, cutting or grinding, some particles may have a diameter of less than 0.05mm. Material less than 0.05mm will usually need to be removed from the particles to maintain permeability during use but need not be discarded..

The fine material removed following crushing, grinding or cutting can also be pelletised by pressing the homogeneous mixture into pellets using a hydraulic press, or by using compression rollers, or a prilling machine, or any other similar means determined to be convenient or efficient. Pressed pellets that are strong and stable enough to survive transport and moderately rough handling can be readily formed using an applied compression of about 50 MPa or more. However, an applied compression of greater than about 150 MPa is preferred and an applied compression of greater than about 250 MPa is still more preferred. Applied compression of about 50, 100, 150, 200, 250, 300, 350 or 400 MPa, or between about 50 and 500 MPa, or between about 100 and 450 MPa, or between about 150 and 400 MPa or between about 200 and 350 MPa may be used. Strong and stable pellets may also be produced from a damp slurry that has been prepared by adding water to the homogeneous mixture. At a suitable moisture content pellets can be prepared by rolling the mixture with little or no compression; commercially available pellet binders (used in the chemical, pharmaceutical, or similar industries; for example methylcellulose or other cellulose derivatives) can be added to the mixture to provide additional physical strength if desired.

The composition according to the invention may be used in several permeable water treatment systems, including water quality management barriers, subsurface reactive barriers, and filtration columns.

Water Quality Management Barriers

The composition according to the invention may be used to make permeable barriers that may be placed in creeks or drains to neutralise acid and remove metals, metalloids and some other potential contaminants (e.g. cyanide and phosphate) from water in the creeks or drains without stopping water flow. As the water flows through the water quality management barrier in the water course, its quality is substantially improved.

The composition according to the invention may be packed in porous bags or similar containers that may be placed in the water course as required. A preferred container is in the form of a geotextile bag with a fine pore size (<5 microns), but other materials could also be used to construct the containers.

The barriers may be constructed in any size or shape, including the following:

- A) Bags shaped like pillows that hold between 15 kg to 30 kg of pellets; these are like sand bags that are used in flood management. The bags may be larger or smaller as required, but this is a convenient size for installation by hand where necessary. These bags may be suitable for temporary placement in small drains or water courses.
- B) Bags shaped like sausages and designed to hold 15 kg to 50 kg or more of pellets made of the composition according to the invention. There is no limit on the size but larger sausages may be more difficult to place in position and may require the use of lifting machinery. These bags may be suitable for use in larger water courses or for making an emergency barrier to surround a spill or unintended discharge of contaminated water.
- C) Elongate bags may be provided with a trapezium shaped cross-section and a length designed to extend from one side of a drain or water course to the other and are pinned to the bottom of the water course. Bags with this design may be suitable for more permanent use in drains or water courses where the water flow volume is highly variable. These bags may be suitable to treat the water when flow rates are low and contaminant concentrations are high. When flow rates are low and contaminants are highly diluted, water treatment is less important and under these circumstances the water will simply flow over the top of the water quality management barrier without reducing the acid neutralising or contaminant trapping capacity of the composition in the bags. Thus water may be treated when necessary and not when discharge conditions make treatment unnecessary.

Bags containing the composition according to the invention may be kept at sites close to where they might be needed in the event of a spill of contaminated water or where some form of emergency response to the release of acidic metal-contaminated water may

become necessary. In the latter sense, the bags may be used like the barriers stored for rapid response to an oil spill. The hydraulic conductivity of the water quality management barriers is important. The ingredients of the composition according to invention and the process steps for processing the ingredients may be selected such as to meet the requirements of an individual application.

Because the water treating capacity of the composition according to the invention is limited, where the composition is used in long term applications, the performance of the composition needs to be monitored. Where the acid or metal removal capacity of the composition becomes depleted it will need to be replaced.

Monitoring can involve the checking of downstream water quality or sub-sampling the contents of the bags and testing the residual acid neutralising and metal binding capacity of the composition in the bag. Depending on the type of contaminants being trapped, once the water treating capacity of the composition is exhausted, the composition may often be suitable for reuse in agriculture as a soil conditioner or improver, thereby reducing the cost of replacing the composition in the bags.

Sub-surface Permeable Reactive Barriers

The composition according to the invention may be used to provide permeable sub-surface reactive barriers that may be placed in ground to neutralise acid and remove metals, metalloids and some other potential contaminants (e.g. cyanide and phosphate) from sub-surface waters, without impeding water flow. As the sub-surface water flows through the permeable sub-surface reactive barrier, the quality of the sub-surface water is improved.

Sub-surface reactive barriers or treatment walls may involve the construction of permanent, semi-permanent, or replaceable sections of walls or barriers, each comprising containers holding pellets of the composition according to the invention. The walls or barriers may be provided across the flow path of a ground water borne contaminant plume. Where a sub-surface reactive barrier comprising the composition according to the invention is to be replaceable, then a geotextile lining of the treatment zone may be provided to confine pellets to the treatment zone to assist in their removal. The pellets of the composition may be contained within a single geotextile liner that occupies the whole of the treatment zone. The barrier or wall may alternatively be or comprise geotextile bags as described previously. The bags may be stacked within the treatment zone to form a sub-surface reactive barrier.

Contaminated ground water may move passively through the sub-surface reactive barrier, because of a hydraulic gradient, and the contaminants in the water may be removed by physical, chemical and/or biological processes. Depending on the contaminant in the ground water to be treated, reactions may occur by precipitation, sorption, oxidation or reduction, fixation or degradation.

Sub-surface reactive barriers have several advantages to the conventional pump-and-treat methods for ground water remediation because contaminant treatment is occurring in-situ, without the need to bring the water to the surface. In addition, the treatment according to the invention does not require a continuous input of energy to run the pumps, because the natural hydraulic gradient is used to carry the contaminants through the reaction zone. Also, only periodic replacement or rejuvenation of the sub-surface reactive barrier is required should it become exhausted, or clogged during the barrier life time.

Barriers are conveniently designed to have a capacity to treat large volumes of contaminated groundwater. In some situations, because of costs, barriers may be installed that only treat a portion of the total problem. When the treatment capacity of the barrier has become depleted, it may be simpler and cheaper to rather emplace a new barrier slightly up flow of the failing barrier than to excise and replace it. In that way the costs of a treatment program may be spread out over a number of years.

To emplace a sub-surface barrier, a simple trench may be excavated across the groundwater plume and backfilled with the reactive material. The trench may be dug using specialist trenching equipment. The dimensions of the trench may be based on the permeability of the reaction material, the permeability of the surrounding geological materials, the required residence time for contaminant removal reactions to occur within the barrier, the concentration of contaminant in the influent water, the width and depth of the contaminated ground water plume, and the design life of the sub-surface reactive barrier. In addition, other earth works may be provided to direct the ground water flow to the reactive barrier (eg a funnel and gate system). The permeability of the barrier according to the invention may be controlled by increasing or decreasing the particle size of the composition.

An exemplary industrial implementation of a sub-surface permeable reactive barrier is described below with reference to figure 9.

Filtration/Reaction Columns or Tanks

The composition according to the invention may be used to pack a permeable column or tank to neutralise acid and remove metals or metalloids and some other potential contaminants (e.g. cyanide and phosphate) in water, without severely impeding
5 water flow.

The water may be an industrial effluent, a contaminated drinking water or an acid mine drainage water.

The water may be passed through the column or tank under gravity (either as a direct feed or by siphon), be pumped through the column, or be sucked through the column
10 or tank under vacuum. As the water flows through the permeable column or tank, its quality may be substantially improved.

A filtration/reaction column or tank in accordance with the invention may be a column or tank comprising the composition according to the invention. The filtration/reaction column or tank may be a suitable tube packed with the composition
15 according to the invention. The water may be passed from one end to the other to effect the removal of a particular contaminant. Contaminants may be removed because of precipitation, sorption, oxidation or reduction, fixation or degradation reactions, or may be removed because they are attached to suspended particles within the water, which are removed by the pellets by physical separation because they cannot pass through the
20 interconnecting pore spaces. Columns or tanks may be constructed from almost any material, including bamboo, pvc pipe, polyethene drums, stainless steel pipe, and polycarbonate tubing, or any other suitable material. At least one end should be capped to hold the filtration/reaction media within the container. The advantages of using filtration/reaction column or tank, are that the filtration/reaction media are readily
25 replaced when overloading occurs, it is easy to monitor flow rates through the system to determine if physical clogging is occurring, the flow rates and retention times are readily adjusted, effluent water quality is easy to monitor, columns or tanks can be constructed to any desired height and diameter, and they may be engineered to allow back-flushing as required.

30 Because the filtration/reaction media within the filtration/reaction column or tank is in contact with a ridged tube edge, some preferential flow paths may develop between these boundaries. In addition very fine grained media are less desirable in filtration/reaction columns or tanks, because there is a propensity for fine grained media to clog. To overcome these problems the grainsize of the pellets in the column or tank is

limited by the internal diameter of the column or tank, such that the pellets should have a grain size of less than $1/10^{\text{th}}$ of the internal diameter of the column or tank. In addition, treatment in the column or tank is most effective when the pellet grainsize is less than $1/50^{\text{th}}$ of the internal diameter of the column. However, to prevent substantial clogging of the filtration/reaction media, greater than 80% of the pellets should be coarser than 100 μm and preferably greater than 90% of the pellets should be coarser than 100 μm and more preferably greater than 95% of the pellets should be coarser than 100 μm and most preferably greater than 98% of the pellets should be coarser than 100 μm .

To prevent clogging of the filtration/reaction media, pre-filtering of suspended particles in the influent water can be achieved using a coarse-grained sand and gravel filter, which may be back-flushed to remove accumulated material. When overloading of the Treated red mud pellets occurs, the filtration/reaction columns may simply be dismantled the pellets extracted, replaced and disposed of. For an industrial plant several columns can be used in series and/or in parallel, so that fresh columns are available to treat effluent when others be come overloaded.

An exemplary industrial implementation of a process for treating water containing contaminants is described below with reference to figure 8.

Other applications of the Composition according to the Invention

Pellets of the composition according to the invention may be used as gravel in a fish tank, ornamental pool or other water body, to remove nutrients or to prevent excessive algal growth.

In another embodiment of the invention, bags of pellets of the composition in accordance with the invention may be suspended in a water body or may be formed as a floating island to treat the water.

Mobile and stationary water treatment tanks may be provided, and the tanks may be filled with pellets of the composition according to the invention, to treat water either continuously or as required.

Alternatively, coarse gravel or cobble sized pellets may be placed directly in a flowing water body (e.g. in a creek), to neutralise acid or to remove metal contaminants.

The invention also extends to the provision of a column for the treatment of a gas containing a potentially acid forming substance such as an oxide of sulphur and/or nitrogen, or for the treatment of a gas to remove polar organic molecules.

In another embodiment of the invention, a porous pellet blanket, made of the composition in accordance with the invention is provided to control odour emissions.

Thus, by following the teachings of the present invention, stable, strong and porous particles of a composition comprising red mud can be made. These particles may be in the form of pellets, and they may have and retain a large surface area as well as a high acid neutralising metal binding capacity. The intrinsic permeability of these particles may allow flowing water to pass through and around the material. When dry, the dust forming propensity of these particles is low.

10 EXAMPLES

Example 1: Scanning Electron Microscope investigation of internal porosity of developed pellets

Two pellets were made using the following methodology.

Pellet 1 was made by mixing the following components to form a slurry

- 15 80 g treated red mud
- 4g hydrated lime
- 4g magnesium oxide
- 2 g HPMC plasticiser/polymeriser,
- 15 g portland cement;
- 20 8 g silica sand of dry ingredients
- 70 mL of water,
- 8 mL of 3% H_2O_2 , and
- 0.22 mL of 1.5M H_3PO_4

The above components were mixed in a shear-force mixer for one minute. The wet slurry was poured into a mould with a height to diameter aspect ratio of 3.5:1 and was restrictively capped and allowed to cure for 28 days.

Pellet 2 was made by mixing the following components to form a slurry:

- 70 g treated red mud
- 30 2 g HPMC plasticiser,
- 15 g Portland cement,
- 13 g of silica sand
- 70 mL of water,
- 0.8 mL of 3% H_2O_2 , and

0.22 mL of 1.5M H_3PO_4 ,

The above components were mixed in a shear-force mixer for one minute. The wet slurry was poured into a mould with a height to diameter aspect ratio of 3.5:1, which was restrictively capped and allowed to cure for 28 days.

After 28 days the moulds were opened and samples of the pellets inspected under the scanning electron microscope, to investigate the fine textural, and structural characteristics.

The attached SEM images show the porous nature of the pellets and the lattice network of fine grained minerals making up the structure, and the presence of acid neutralising minerals within pore spaces that developed during pelletisation.

Figure 1 is an SEM image of pellet 1 showing the distribution of macro-pores developed during the pelletisation process.

Figure 2 shows the fine pore detail in pellet 1. It can be seen from Figure 2 that the pellets have a highly distributed pore size. The macro-pore size is on the order of 20 to 100 μm in size and micro-pores on the order of 0.2 μm to 1 μm connect between them, through the walls. Macro-pore sizes of up to 2000 μm have been achieved in other experimental results.

Figure 3 shows the detail of the pore sides showing the fine interconnected tobermorite gel of the pellet 1. Large rhombohedral crystals are CaCO_3 , crystallised from the pore water during curing.

Figure 4 shows the collapsed tops of 2 carbonate filled macro-pores.

Figure 5 shows an SEM image of pellet 2 showing the distribution of macro-pores developed during the pelletisation process.

Figure 6 is a high resolution image of the surface of pellet 2, showing the micro-pore network that permeates the pellet.

Example 2: Treatment of a metal-rich tannery effluent using a column constructed of porous pellets

Referring to Figure 7, there is shown a schematic diagram of laboratory apparatus that was use to obtain the results of example 2. This trial used pellet 1, as given in Example 1 above, which was lightly crushed and sieved to give material in 4 grainsize ranges, of 250 μm to 500 μm , 500 μm to 750 μm , 750 μm to 1000 μm , and 1000 μm to 2000 μm . A pellet mix each of 25% of each of the 4 grainsizes was made to provide the filtration/reaction column (10). Three filtration/reaction columns (10, 20, 30) were

constructed using polycarbonate tubing with an internal diameter of 44 mm. Each column (10, 20, 30) was sealed at one end and was packed with a 10 cm long coarse sand and gravel mixture (12) to act as a pre-filter, a geotextile wadding, a 5 cm long section of treated red mud pellets (14) another geotextile wadding (16), an other 10 cm long coarse sand and gravel pack to hold the treated red mud pellets (14) in place. The filtration/reaction columns (10, 20, 30) were and set up in series with a settling/precipitation vessel (22, 24) between each column

The tannery effluent was drawn through the columns under a 600 Mpa vacuum (26) where it was collected in a settling/precipitation vessel (32) for analysis and comparison to data for the direct addition of treated red mud to the same effluent. The total mass of treated red mud pellets in the reaction/filtration columns (10, 20, 30), was equal to the quantity of treated red mud added in a direct addition experiment. Effluent analysis, direct addition results and reaction/filter column results are presented in Table II below. Table II presents data from the treatment of tannery effluents using developed porous pellets, in a filter tube (reaction column).

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Table II.

Results for the direct addition of treated red mud to a tannery effluent, and the treatment of the same effluent using pellet 1 of example 1

Parameter	Raw Effluent	Direct addition	Direct Addition Removal %	Column	Column Removal %
pH	2.41	8.06	-	8.03	-
TSS (mg/L)	490	47	90.44	5	98.98
BOD (mg/L)	327	118	63.88	29.4	91.01
Total P (mg/L)	3.54	0.160	95.47	0.063	98.22
Total N (mg/L)	59.52	14.06	76.37	20	66.40
Na (mg/L)	810	824	-1.71	538	33.58
K (mg/L)	817	1388	-69.93	26.3	96.78
Mg (mg/L)	1520	7757	-410.34	902	40.66
Ca (mg/L)	186	506	-172.13	460	-147.31
Sulphate (mg/L)	9310	7237	22.26	3390	63.59
Chloride (mg/L)	1844	1198	34.99	992	46.20
Al (mg/L)	384	0.134	99.97	0.0001	99.99997
Cr (mg/L)	53.7	0.33	99.39	0.0009	99.998
Cu (mg/L)	16.2	0.014	99.91	0.008	99.95
Fe (mg/L)	106	0.542	99.49	0.0002	99.9998
Mn (mg/L)	96.7	9.35	90.33	4.260	95.59
Ni (mg/L)	9	0.089	99.01	0.023	99.74
Zn (mg/L)	21.7	0.132	99.39	0.046	99.79

TSS denotes total suspended solids and BOD denotes the 5 day biochemical demand.

Example 3: Directions for making batches of porous pellets in a 4 m³ cement mixer

Ingredients

- 5 2000 kg of A1 treated red mud screened to <2 mm
- 400 kg of ordinary portland cement:
- 250 kg of finely ground silica sand:
- 100 kg of hydrated lime screened to <1 mm:

200 kg of magnesium oxide screened to <1 mm:

50 kg of hydro-propyl methyl cellulose (HPMC) plasticiser:

About 2000 L of water:

25 L of 3% hydrogen peroxide (H_2O_2):

5 7 L of 1.5 M orthophosphoric acid (H_3PO_4):

Total weight of dry products: 3,000 kg

Total weight wet products: about 2,032 kg

Total wet weight: about 5,032 kg ($2m^3$)

It should be appreciated that it is optional to use dry treated red mud as indicated
 10 above. Treated red mud with a moisture content of about 50% could be used instead, but
 the amount of water to be added would need to be reduced in direct proportion to the
 amount of water included with the treated red mud. Washed treated red mud is not
 required but the treated red mud must be treated. For example, if the treated red mud to
 15 be used is supplied as a 50% slurry only the dry additives and a small amount of water
 would be required. Using the treated red mud as a screened slurry would eliminate the
 time and cost associated with drying it and could thereby overcome the main bottleneck in
 treated red mud production.

The ingredients above are for production of a general purpose treated red mud C5T10
 blend. Other blends can be produced but mixtures may need to be adjusted carefully and
 20 a small amount of hydrated lime and magnesium oxide may need to be retained to ensure
 that a calcium or magnesium deficiency or a high sodium to calcium plus magnesium
 ratio does not adversely affect setting characteristics.

Example 4: Process steps for making pelletised composition.

25 **Step 1:** Add 400 L of water to the mixer then add 2 t of the screened treated red mud and
 allow it to mix until a dry paste has formed.

Step 2: While mixing, dilute 1 L of phosphoric acid with 10 L of water, add it to mixer
 and allow mix for 15 mins.

Step 3: Add 400 kg of cement to the mixer and mix for 15 mins with an additional 400 L
 30 of water. A small amount of detergent can be added to improve for lubrication if
 necessary.

Step 4: While continuing to agitate the main ingredients, vigorously mix 200 kg of
 magnesium oxide and 100 kg of hydrated lime with 300 L of water in an IBC for 10 mins.

Step 5: Add the pre-mixed lime and magnesium oxide to the main mixer and allow to mix for 10 mins.

Step 6: While continuing to agitate the ingredients, mix 25 kg of HPMC with 150 L of hot water in an IBC and mix vigorously for 5 mins and then dilute to 300 L and mix for a
5 further 5 mins.

Step 7: Add the pre-mixed polymer to main mixer and allow to mix for 10 mins .

Step 8: Repeat steps 6 and 7

Step 9: Add water (<300 L depending upon treated red mud water content) to the mixture until the desired consistency is achieved (a simple indicator test is currently being
10 developed).

Step 10: While continuing mixing, dilute 2 L of the hydrogen peroxide with 23 L of water, add the diluted hydrogen peroxide to mixer and mix for 5 mins.

Step 11: Pour the mixture into slab between 100 mm and 200 mm thick; formwork should be set up in advance to hold the desired quantity of mix.

Step 12: Allow poured slab to gel for 3-6 hours and then stamp it into long rectangular blocks that can easily be lifted and stacked until cured and required for crushing.
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Step 13: Allow stamped blocks to set for 7-10 days before stacking for final curing.

Step 14: Allow stacked blocks to cure for another 21 days minimum if using impact crushing or another 7 days if using a cutter (e.g. a wood chipper) to break the slab into
20 pellets.

Industrial applications

The pellets made as described in any one of the examples 1 to 4 above can be used in an industrial process to remove contaminant from fluids that contain
25 contaminants.

An exemplary industrial application is shown in figure 8, which shows a schematic diagram of an industrial process (100) to treat contaminated water. The process (100) includes a feed tank (105) that holds contaminated water. The feed tank (105) supplies the contaminated water via a feed line to a train of contaminant removal tanks (110, 120, 130). Each of the contaminant removal tanks (110, 120, 130) are packed with a
30 permeable mass of pellets (110', 120', 130') that are made as described in any one of the examples 1 to 4 above. The permeable mass of pellets (110', 120', 130') when packed within the contaminant removal tanks (110, 120, 130) have a porosity ϵ of about 60%. The permeable mass of pellets (110', 120', 130') are packed between two sand porous

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contaminant flow rate may be altered according to the concentration of contaminant in the

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particles down stream.

While this invention has been described in specific detail with reference to the disclosed embodiments, it will be understood that many variations and modifications may be effected within the spirit and scope of the invention as described in the appended claims.

5

Dated 23 December, 2003

Virotec International Ltd

Patent Attorneys for the Applicant/Nominated Person

SPRUSON & FERGUSON

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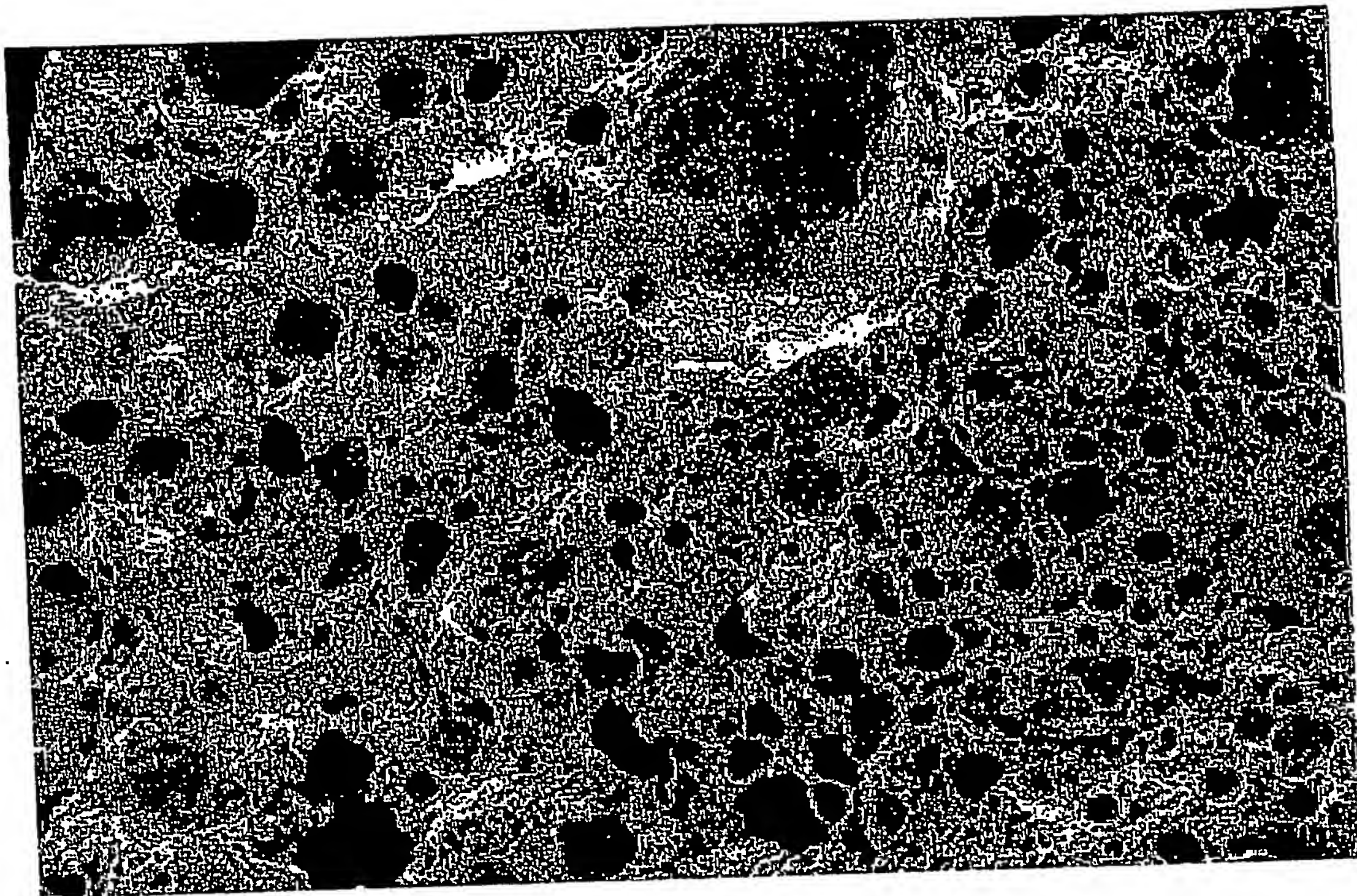


Figure 1

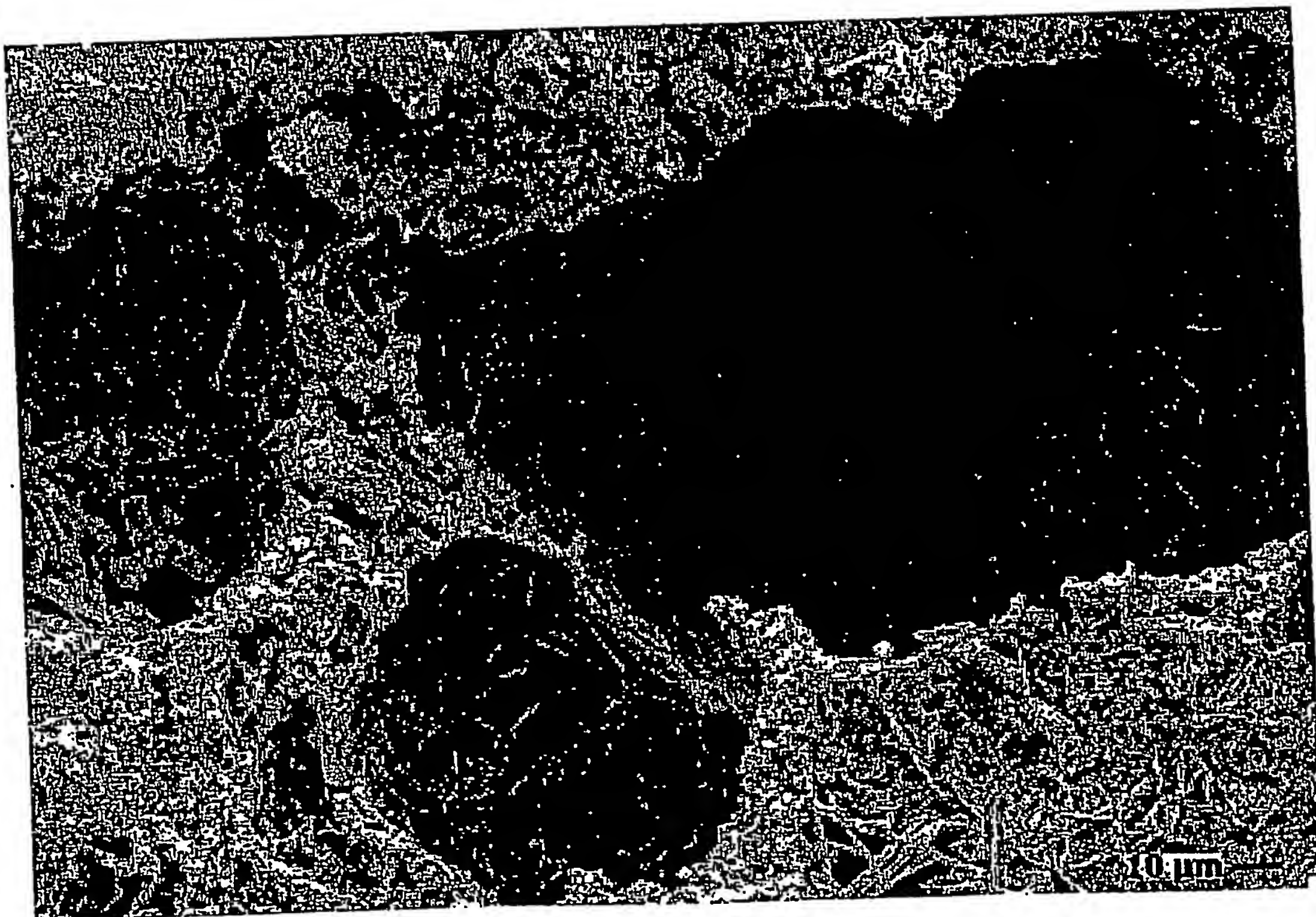


Figure 2

2/6



Figure 3

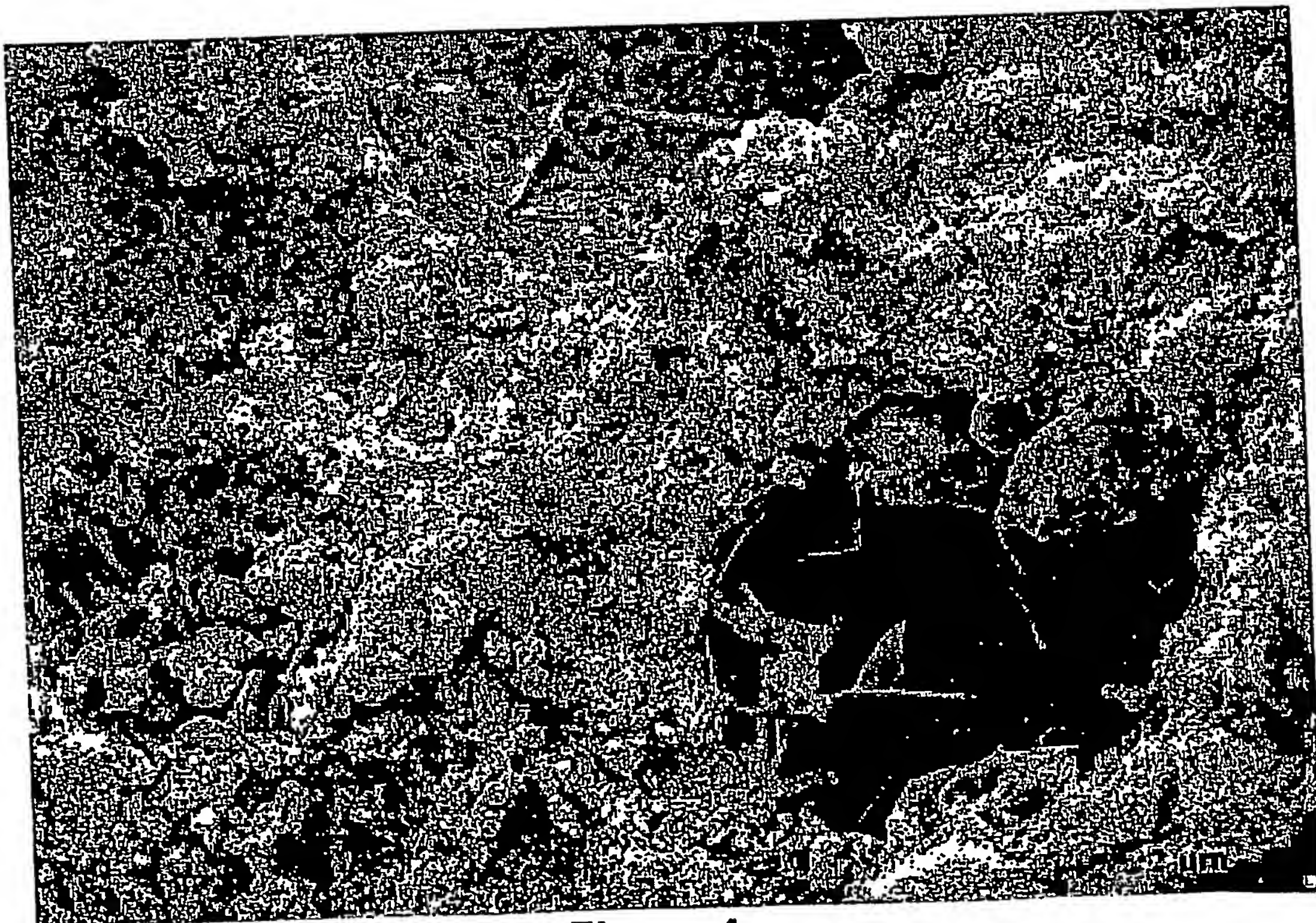


Figure 4

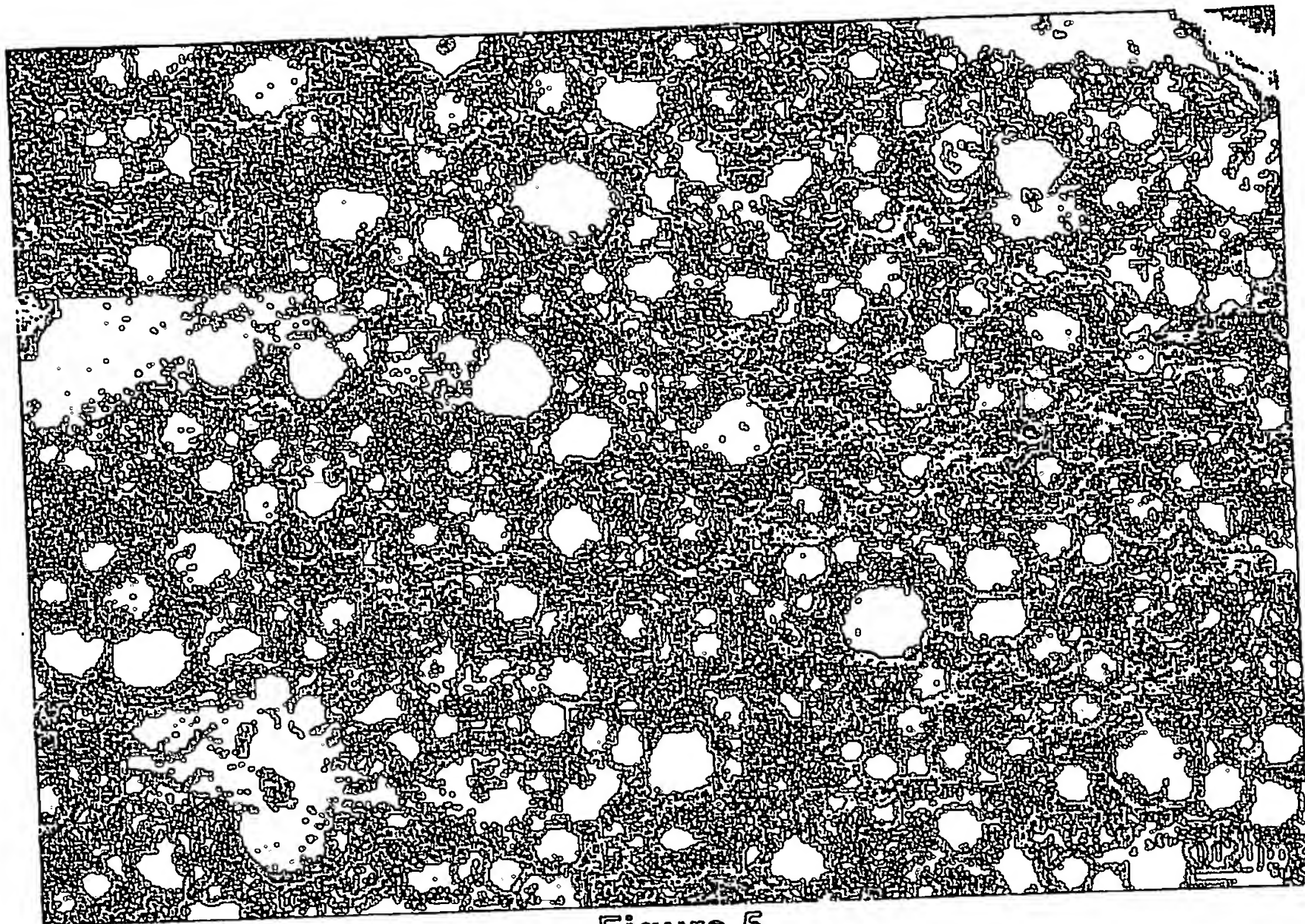


Figure 5

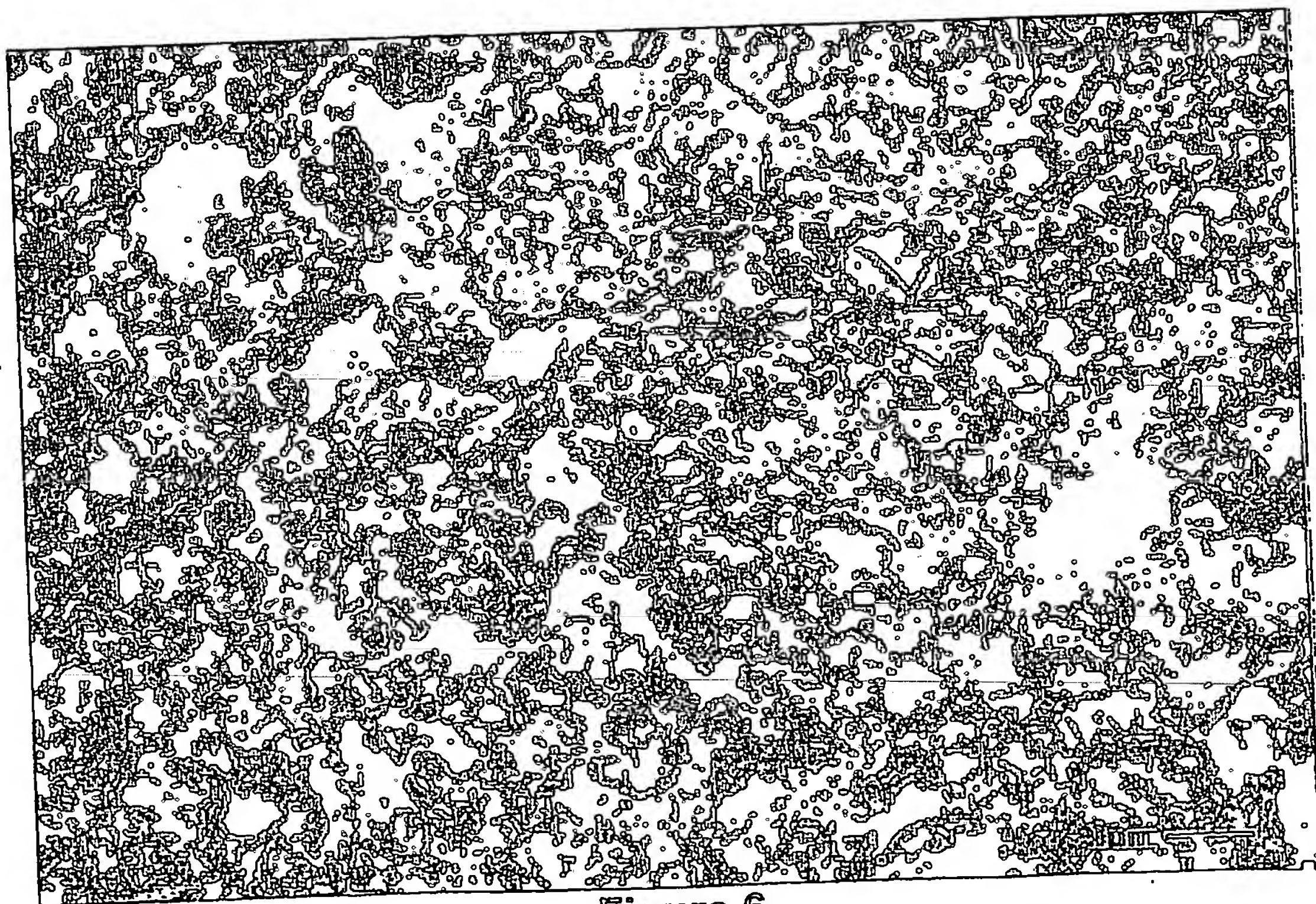


Figure 6

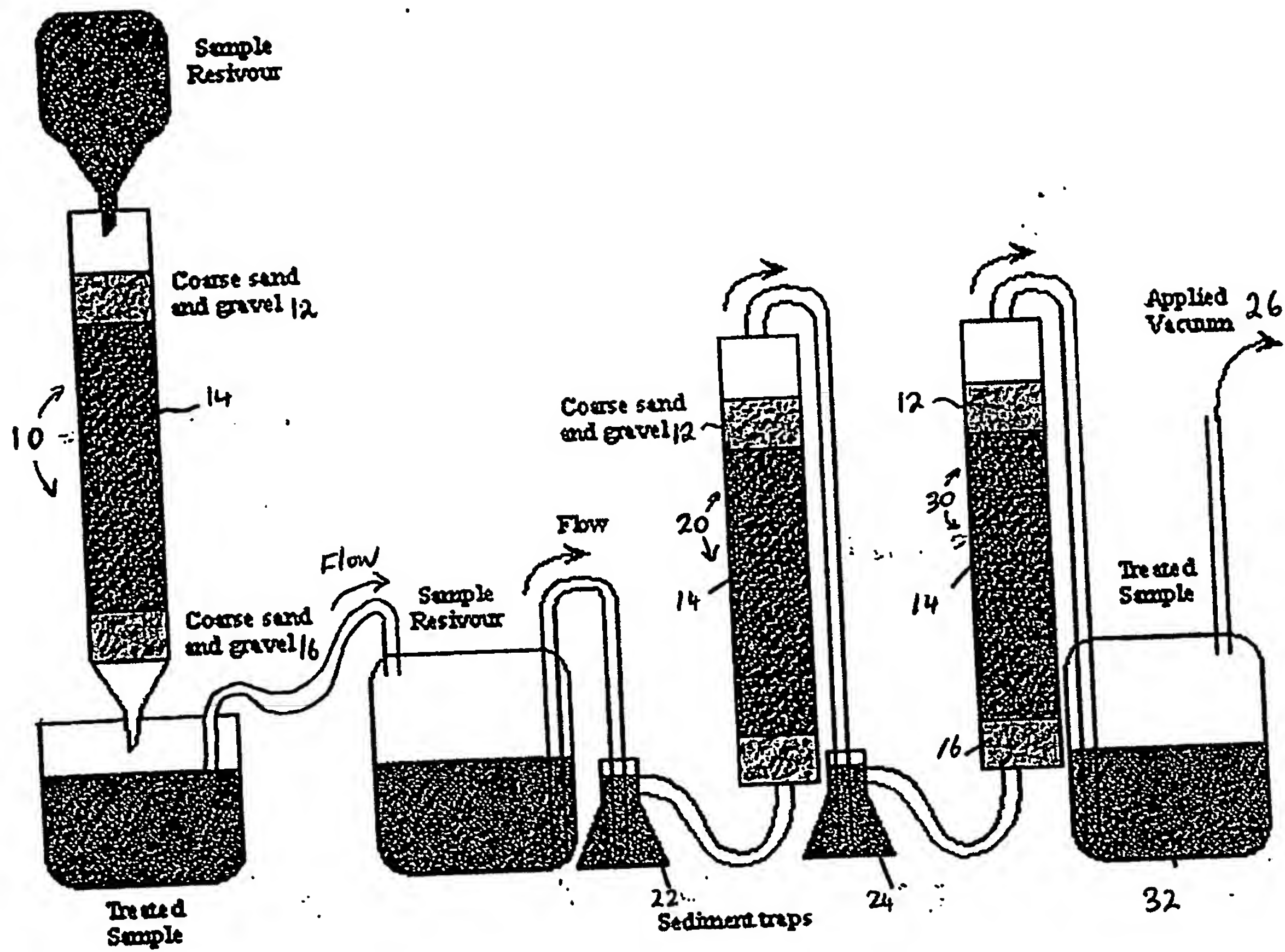


FIGURE 7

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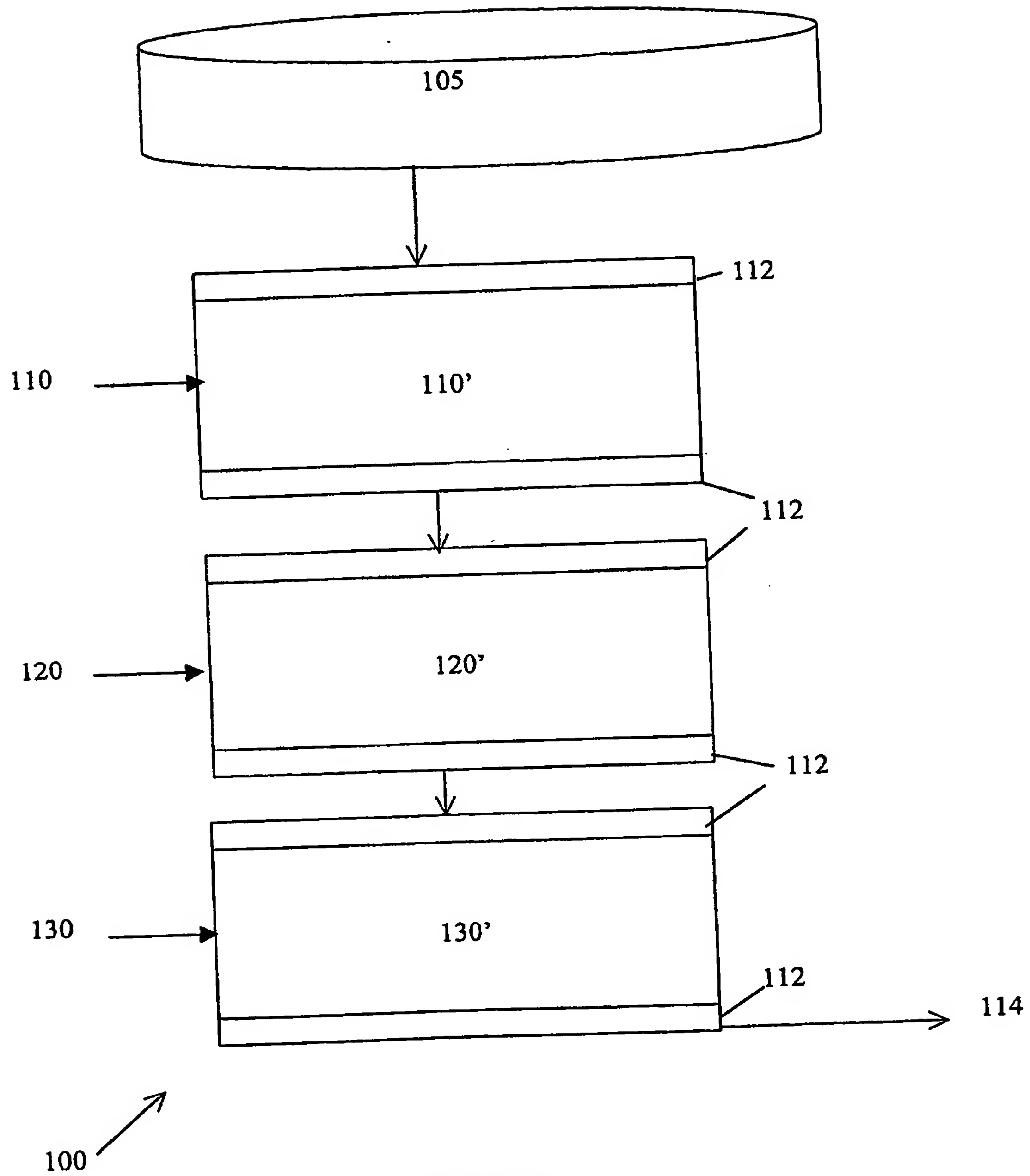
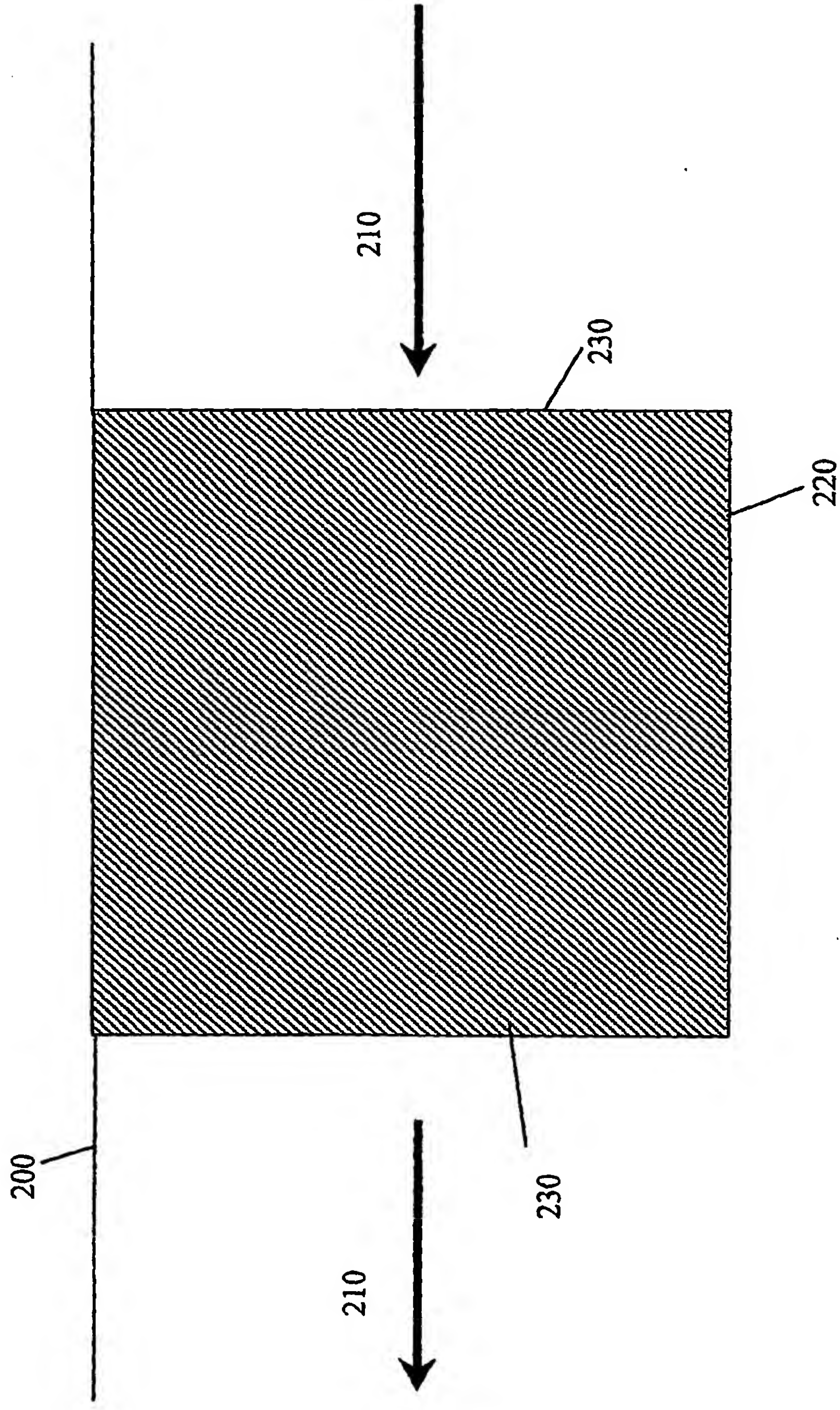


FIGURE 8



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FIGURE 9

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